

Power Dependent Lineshape Corrections for Quantitative Spectroscopy

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(Dated: February 26, 2013)

The Voigt profile – a convolution of a Gaussian and a Lorentzian – accurately describes the absorption lines of atomic and molecular gases at low probe powers. Fitting such to experimental spectra yields both the Lorentzian natural linewidth and the Gaussian Doppler broadening. However, as the probe power increases saturation effects introduce spurious power dependence into the fitted Doppler width. Using a simple atomic model, we calculate power-dependent corrections to the Voigt profile, which are parametrized by the Gaussian Doppler width, the Lorentzian natural linewidth, and the optical depth. We show numerically and experimentally that including the correction term substantially reduces the spurious power dependence in the fitted Gaussian width.

Vapour cell spectroscopy is important for determining the properties of atomic or molecular transitions [1, 2], which are well described by the Voigt profile, the workhorse of transmission spectroscopy. Experimental progress has reached the point that intensity dependent corrections to the Voigt profile are becoming significant. For example, molecular fingerprinting and other trace gas measurement applications [3, 4] using direct frequency comb spectroscopy (DFCS) [5] require a quantitative link between absorption depths and gas concentrations, particularly if the probe laser intensity levels are increased to improve signal-to-noise in challenging environments. While absorption sensitivities measured using DFCS can be determined with quantum-noise limited precision [6], the effects of optical pumping on the observed depths and line-shapes remain to be quantified. Similarly, optical pumping can limit accurate determinations of the Boltzmann constant, k_B , from measurements of Doppler-broadened line shapes [7–13]. To optimise the trade-off between signal-to-noise limitations at very low powers, and systematic optical pumping effects at higher powers, an accurate theory of the line shape dependence on probe intensity is needed.

In the limit of low probe powers, where atomic populations are hardly perturbed from their thermodynamic equilibrium values, transmission spectra are well described by an exponentiated Voigt function [14, 15], $\mathcal{T}_{\text{lin}}(z) = e^{-\alpha z V_\nu(\Delta)}$, where α is the absorptivity, z is the length of the vapour cell, Δ is the detuning from resonance (note: all times and frequencies are expressed in units of $\Gamma = \Gamma_{\text{natural}}/2$), $\nu = \gamma/\Gamma$ is the non-dimensional Doppler width, and V is a convolution of a Gaussian and a Lorentzian:

$$V_\nu(\Delta) \equiv \frac{1}{\pi^{3/2}\nu} \int_{-\infty}^{\infty} \frac{e^{-(x-\Delta)^2/\nu^2}}{1+x^2} dx, \\ = \text{Re}\{e^{-(i+\Delta)^2/\nu^2} \text{erfc}(-i(i+\Delta)/\nu)/(\sqrt{\pi}\nu)\},$$

where $\text{erfc}(z) = 2 \int_z^\infty e^{-t^2} dt/\sqrt{\pi}$.

At low probe powers, \mathcal{T}_{lin} describes the measured

transmission spectrum very accurately; the Gaussian component arises from the Doppler shifts due to the atomic Maxwell-Boltzmann velocity distribution, while the Lorentzian relates to atomic relaxation processes. Fitting \mathcal{T}_{lin} to experimental measurements yields γ , Γ and the optical depth. However, as the probe power increases, perturbations to the equilibrium atomic population distribution become significant and \mathcal{T}_{lin} fails to accurately represent the transmission spectrum. In the limit of large probe powers, atomic populations depart from thermodynamic equilibrium: in two level atoms the ground and excited states tend to equalise; in three level systems population may be transferred to an optically inactive state. In either case, fitting \mathcal{T}_{lin} to the measured spectrum yields incorrect values for γ and Γ , which acquire a spurious intensity dependence.

In this letter, we derive the intensity dependent corrections to \mathcal{T}_{lin} , which can be computed perturbatively in powers of the laser intensity. We then show, both theoretically and experimentally, that fitting to the corrected form yields Doppler widths that are independent of intensity as they should be. This result will enable accurate measurements of Doppler broadening in quantitative spectroscopy at much higher probe intensities, where saturation effects are not negligible. This in turn greatly enhances signal-to-noise in a given integration time.

We begin by computing the spectral dependence on the atomic populations for a three level atom, consisting of two ground states: one optically active, $|1\rangle$, and the other optically inactive, $|2\rangle$, and an excited state $|3\rangle$, as discussed in [16]. Transitions between states $|1\rangle$ and $|3\rangle$ are optically driven, and state $|3\rangle$ can relax to either of the ground states. The population rate equations are

$$\frac{d\vec{P}}{dt} = M \cdot \vec{P}, \quad M = \begin{pmatrix} \frac{\Omega^2/2}{1+\Delta^2} & 0 & 2\beta + \frac{\Omega^2/2}{1+\Delta^2} \\ 0 & 0 & 2(1-\beta) \\ -\frac{\Omega^2/2}{1+\Delta^2} & 0 & -2 - \frac{\Omega^2/2}{1+\Delta^2} \end{pmatrix}, \quad (1)$$

where $\vec{P} = \{P_1, P_2, P_3\}$, Ω is the atomic Rabi frequency (proportional to the electric field amplitude), β is the

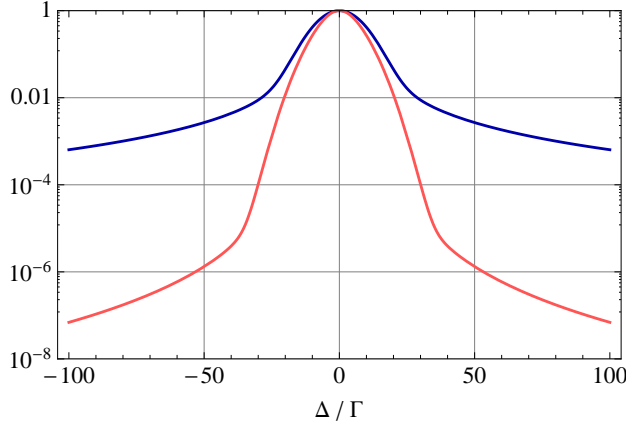


FIG. 1. (Colour online) Typical form for the Voigt function (dark, blue), and the correction term multiplying \tilde{q} in Eq. (6) (light, red), for $\nu = 10$, $\tilde{p} = 20$.

branching ratio from state $|3\rangle$ to $|1\rangle$ and Δ is the detuning between the laser frequency and the atomic transition.

The light is absorbed as it propagates through the atomic medium, and the axial evolution of the field is governed by [16]

$$\frac{\partial \ln \Omega^2}{\partial z} = 2\alpha \int_{-\infty}^{\infty} d\Delta_{v_z} \frac{e^{-(\Delta - \Delta_{v_z})^2/\nu^2}}{1 + \Delta_{v_z}^2} P(\Delta_{v_z}). \quad (2)$$

Here $P(\Delta_{v_z}) = P_3(\Delta_{v_z}) - P_1(\Delta_{v_z})$ and the notation Δ_{v_z} indicates that a given atom sees a detuning which depends on its axial velocity via the Doppler shift. If the field intensity is weak, so that on resonance populations are negligibly perturbed from thermal equilibrium, then $P = -1/2$, and the integral yields $\Omega^2(z) = \Omega_0^2 e^{\alpha z V_\nu(\Delta)}$. Since $\mathcal{T}(z) = \Omega^2(z)/\Omega_0^2$, we recover $\mathcal{T} = \mathcal{T}_{\text{lin}}$.

As Ω^2 grows, perturbations to P become significant, and we should compute corrections to P using Eq. (1). In the simplest case where Ω^2 is time-independent Eq. (1) can be solved analytically. The expression is cumbersome, however it may be straightforwardly expanded in powers of Ω^2 to yield

$$P(\Delta_{v_z}) = -\frac{1}{2} + q(t) \frac{\Omega^2}{1 + \Delta_{v_z}^2} + O(\Omega^4), \quad (3)$$

where $q(t) \approx (1 + \beta + 2t(1 - \beta))/8$, and t is the time for which the atom is exposed to the field. Substituting this result into Eq. (2) yields

$$\frac{\partial \ln \Omega^2}{\partial z} = -\alpha V_\nu(\Delta) + \alpha q(t) V_\nu^{(2)}(\Delta) \Omega^2 + O(\Omega^4) \quad (4)$$

where

$$V_\nu^{(n)}(\Delta) = \int_{-\infty}^{\infty} d\Delta_{v_z} \frac{e^{-(\Delta - \Delta_{v_z})^2/\nu^2}}{(1 + \Delta_{v_z}^2)^n}$$

is a generalisation of the Voigt profile.

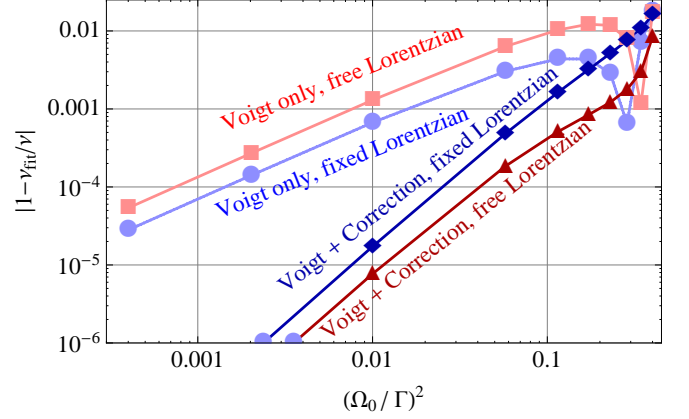


FIG. 2. (Colour online) Fits to numerically simulated spectra, showing the ratio of fitted Doppler to Lorentz widths demonstrate the improved performance of fits using the correction term.

$V^{(2)}$ may be evaluated by noting that

$$\frac{1}{(1+x^2)^2} = \lim_{a \rightarrow 1} \left\{ \frac{a^2}{(a^2-1)(a^2x^2+1)} + \frac{1}{(1-a^2)(x^2+1)} \right\}.$$

Convolving this sum of two Lorentzians with a Gaussian thus yields a sum of Voigt functions,

$$\begin{aligned} V_\nu^{(2)}(\Delta) &= \lim_{a \rightarrow 1} \left\{ \frac{a^2}{(a^2-1)} V_{a\nu}(a\Delta) + \frac{1}{(1-a^2)} V_\nu(\Delta) \right\} \\ &= \text{Re} \left\{ \frac{\nu + \sqrt{\pi} e^{-\frac{(\Delta+i)^2}{\nu^2}} (i\Delta + \nu^2/2 - 1) \text{erfc}(\frac{1-i\Delta}{\nu})}{\pi \nu^3} \right\}. \end{aligned}$$

Higher order correction terms can be calculated iteratively, using the same method.

Equation (4) can be solved analytically to give

$$\mathcal{T} = \frac{e^{-\alpha z V_\nu(\Delta)}}{1 + q \Omega_0^2 V_\nu^{(2)}(\Delta) (e^{-\alpha z V_\nu(\Delta)} - 1)/V_\nu(\Delta)}, \quad (5)$$

Expanding this expression, and recalling that all quantities are nondimensionalised in units of Γ we explicitly include the Lorentz width as a parameter

$$\mathcal{T} \approx e^{\tilde{p} V_\nu(\Delta/\Gamma) + \tilde{q} (e^{\tilde{p} V_\nu(\Delta/\Gamma)} - 1) V_\nu^{(2)}(\Delta/\Gamma)/V_\nu(\Delta/\Gamma)} \quad (6)$$

where $\tilde{p} = -\alpha z$ and $\tilde{q} = -q \Omega_0^2$. This correction, linear in $\tilde{q} \propto I$, is the central result of this Letter. If either the intensity ($\propto \tilde{q}$) is small, or if the optical depth ($\propto \tilde{p}$) is small, the correction vanishes and the well-known Voigt profile is recovered. In the latter case, saturation effects may be substantial, however the optical depth of the sample is sufficiently short that only a small fraction of incident photons are absorbed. In what follows we demonstrate both numerically and experimentally the advantages of using Eq. (6) when fitting spectra for which saturation effects become significant.

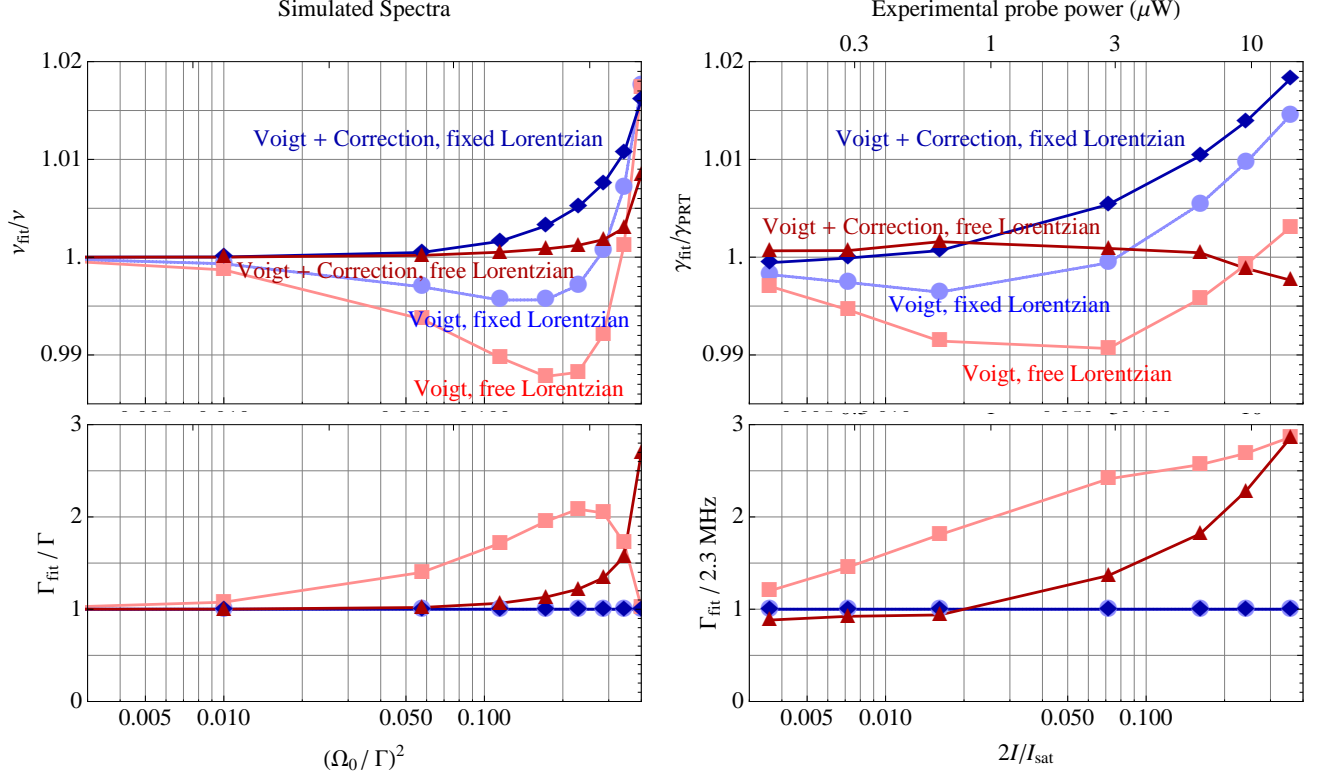


FIG. 3. (Colour online) Fits to (left) Simulated data using Eq. (2), with $\beta = 1/2$, $t = 20$, $\nu = 100$; (right) experimental data taken from [17]. (top) Fitted Doppler widths, extracted from fits to Voigt only or Voigt plus correction, with fixed or free Lorentzian widths. (bottom) Fitted Lorentzian widths, normalised to the natural linewidth.

We note that the derivation of the correction term assumed the Rabi frequency was time independent. However, in an experiment atoms crossing through a probe laser beam see a time-dependent field. Nevertheless, Eq. (3) and (4) are still correct, albeit with some more complicated time dependence in $q(t)$, and taking Ω to represent a typical scale of the local Rabi frequency (e.g. that corresponding to the peak intensity in the probe). It follows that the form of the correction term in Eq. (6) is also valid, where the complicated time dependence in q is simply absorbed into the parameter \tilde{q} .

A typical Voigt profile and the correction are shown in Fig. 1. In fitting to spectra, ν , \tilde{p} and \tilde{q} are treated as fitting parameters. We also numerically investigate leaving Γ free, which heuristically accounts for higher order intensity dependences that we have otherwise neglected; variation in Γ implies a breakdown in the fitting model.

To evaluate the efficacy of the correction, we numerically simulate an absorption spectrum using Eq. (2) (keeping terms in P up to $O(\Omega^6)$), and then attempt to extract the simulation parameters by fitting Eq. (6). For comparison, we compare fits with Voigt only ($\tilde{q} = 0$) and Voigt plus correction (\tilde{q} free); in combination with a fixed Lorentzian ($\Gamma = 0$) and free Lorentzian (Γ free).

Fig. 2 shows the deviation of $\nu_{\text{fit}} = \gamma_{\text{fit}}/\Gamma$ from the correct value, ν , as a function of intensity ($\propto (\Omega_0/\Gamma)^2$), for the different fitting forms. As expected, all fitting forms yield the correct value for ν_{fit} as $\Omega_0^2 \rightarrow 0$. Without the correction (\blacksquare and \bullet), the fit converges to the correct value as Ω_0^2 . This improves to Ω_0^4 when the correction is included (\blacklozenge and \blacktriangle).

The fitting performance is further illustrated in Fig. 3 (left), which shows the dependence of the fitted parameters ν_{fit}/ν (top) and Γ (bottom) as a function of the probe intensity ($\propto (\Omega_0/\Gamma)^2$), for a particular representative choice of parameters ($\beta = 1/2$, $t = 20$, $\nu = 100$). Also shown is the fitted Lorentzian component, Fig. 3 (bottom), demonstrating apparent broadening of the atomic lifetime, even for intensities substantially below the saturation intensity. This phenomenon has been observed experimentally [17].

Qualitatively, at low powers the uncorrected, Voigt-only fits (\blacksquare and \bullet) systematically underestimate ν over a range of laser powers, and demonstrate a pronounced minimum, as illustrated in Fig. 3(top). In the case where the Lorentzian is held fixed (\bullet), the Voigt-only fit may over- or under-estimate the Doppler width, depending on the parameters, i.e. the initial slope may be positive

or negative. For the parameter choices in the simulated spectra, Fig. 3 (left), the initial slope is slightly negative, and there is a noticeable minimum in ν_{fit}/ν .

We now demonstrate the effectiveness of using the corrected transmission function for extracting the true atomic velocity distribution from experimental data. Spectra were recorded in a 7 cm long Caesium vapour cell at approximately 295 K at different probe powers, using a collimated 2 mm diameter laser. At each power setting, 16 spectral scans were taken, and each scan was fitted using Eq. (6) to yields estimates for γ_{fit} and Γ_{fit} . For each scan, the temperature was recorded using a platinum resistance thermometer (PRT), accurate to ± 100 ppm. Each fitted Doppler width, γ_{fit} , was normalised by the width expected given the temperature measured using the PRT, $\gamma_{\text{PRT}} = \omega_{\text{probe}} \sqrt{2k_B T_{\text{PRT}}/m}/c$.

To qualitatively compare the fitting results from the simulated spectra with the experimental results, we convert the laser power to an average intensity by dividing the power by the beam area, $\pi(1 \text{ mm})^2$, and then normalise this average intensity by the saturation intensity $I_{\text{sat}} = 2.51 \text{ mW/cm}^2$ [18], so that the nondimensional experimental parameter, $2I/I_{\text{sat}}$, is equivalent to the nondimensional simulation parameter $(\Omega/\Gamma)^2$.

The results are shown in Fig. 3 (right). For $2I/I_{\text{sat}} < 0.1$, the extracted Doppler widths are substantially better when using the correction than not, as shown in Fig. 3 (right,top). This is in qualitative agreement with the simulated data. For the lowest powers used, the corrected estimates for the Doppler width are at least an order of magnitude better than the uncorrected form, limited by the accuracy of the PRT calibration, and statistical uncertainty from the small sample size.

Comparing Fig. 3 (left) and (right) shows that the simulated results are in qualitative agreement with the experimentally derived results in other respects as well, including the relative locations of minima, slopes and crossing points. Quantitative differences arise from the simplified physical model underpinning the simulated spectra, in which the distribution of atomic crossing times and intensity profiles is replaced by the average crossing time and the average intensity. While not unphysical, this differs from the experimental conditions.

In thermometry, where the objective is to extract very accurate Doppler widths from spectral data, we see from Fig. 2 that it is important to use the Voigt correction. For instance, if $2I/I_{\text{sat}} \sim 0.003$ then a fit to a Voigt-only profile has a systematic bias in the fitted Doppler width at the level of several hundred ppm. In contrast, using the corrected form yields an estimate of the Doppler width that is accurate to ~ 1 ppm, which is comparable to the current thermometric state-of-the-art.

It follows that under the comparable experimental conditions represented in Fig. 3 (right), to reduce the systematic bias in the fitted Doppler width to 1 ppm (when utilising the corrected form), the probe beam should op-

erate at $2I/I_{\text{sat}} = 0.003$, corresponding to a laser power of 100 nW in a 2 mm diameter beam.

One important application of Doppler spectroscopy is to contribute to the CODATA redefinition of Boltzmann's constant [8, 9, 12, 13], in which the vapour cell is at equilibrium with a triple-point-of-water reference at 273.16 K. At this temperature the optical depth of the cell is ~ 10 times smaller than under the experimental conditions reported here. As such, the intensity may be increased by the same factor, to $\sim 1 \mu\text{W}$, while still maintaining the systematic Doppler error at ~ 1 ppm.

In conclusion, we have derived the power-dependent correction to the Voigt profile, and demonstrated numerically and experimentally that including the correction term yields much better estimates of the width of the underlying Gaussian process, substantially reducing the spurious power dependences that arise from an uncorrected Voigt profile. We anticipate that this will find direct application in the near-term to high-precision spectroscopy and thermometry of atomic vapour cells.

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